On statistics and 1/f noise of molecular random walk in low-density gas

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The random walk of test particle in low-density gas is considered basing on approximate coarsened version of the collisional representation of the BBGKY equations. The coarsening presumes that momentum relaxation rates of the test particle and gas atoms are equal but allows to analyze the case when their masses are different. It is shown that both the spectrum exponent and probability distribution of 1/f-type diffusivity fluctuations of the test particle essentially depend on ratio of the masses, and corresponding distribution of its path is found.

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I. INTRODUCTION

In [1, 2] and [3] it was argued (see also [4–9] we argued that kinetics of spatially non-uniform gas does not undergo the Boltzmann equation (or other related and similar equations) even under the low-density or Boltzmann-Grad limit ($\nu \to \infty$, $\delta \to 0$, $\nu\delta^2 = \text{const}$, with ν being concentration of gas particles and δ radius of their repulsive interaction). Instead, an infinite chain of kinetic equations appears - for the one-particle distribution function (DF) plus infinite chain of specific two-particle, three-particle, etc. DFs which represent mean density of pair collisions, density of two connected pair collisions, and so on. Solution of such chains (as well as their rigorous formulation) will be a great challenge for future theory. However, instructive and useful approximate solutions dan obtained already at present [1–3, 7, 10], first of all, for situations when the system (gas or liquid) as a whole is almost equilibrium, and the spatial non-uniformity is rather of statistical than thermodynamical nature. For example, when one considers random walk ("Brownian motion") of a test (or probe, or marked) particle in a fluid.

In [1, 2] and later in [3, 10] we considered (at different approximations) the case when the test particle, or "Brownian particle" (BP), is one of gas atoms. Here we consider the case when BP differs from gas atoms (e.g. is an impurity atom).

II. BASIC EQUATIONS

We star from the Bogolyubov-Born-Green-Kirkwood-Yvon (BBGKY) equations [11] for a molecule (molecular-size "Brownian particle") dissolved in a fluid [4–7]:

$$\frac{\partial F_n}{\partial t} = [\, H_n \,, F_n \,] \,+\, \nu \,\frac{\partial}{\partial \mathbf{P}} \int_{n+1} \Phi_b'(\mathbf{R} - \mathbf{r}_{n+1})\, F_{n+1} \,+$$

$$+\, \nu \sum_{j\,=1}^{n} \frac{\partial}{\partial \mathbf{p}_j} \int_{n+1} \Phi_a'(\mathbf{r}_j - \mathbf{r}_{n+1})\, F_{n+1} \;\;, \qquad (1)$$

where $n = 0, 1, \ldots, ,$ $\Phi'_{a,\,b}(\mathbf{r}) = \nabla \Phi_{a,\,b}(\mathbf{r})$ are "atom-atom" and "BP-atom" interaction forces, and all designations are the same as in [4] or [5]. Since we here again are interested in BP's random walk in (quasi-)equilibrium fluid, the initial conditions will be

$$F_n(t=0) \,=\, \Delta(\mathbf{R} - \mathbf{R}_0)\, F_n^{(eq)}(\mathbf{r}^{(n)}\,|\mathbf{R};\nu) \times \\ \times\, G_M(\mathbf{P}) \prod_{j\,=1}^{n} G_m(\mathbf{p}_j) \;\;, \qquad (2)$$

where $F_n^{(eq)}(\mathbf{r}^{(n)}\,|\mathbf{R};\nu)$ are usual thermodynamically equilibrium DF for n atoms in presence of BP occupying point $\mathbf{R}$,

$$G_m(\mathbf{p}) \,=\, (2\pi T m)^{-\,3/2} \exp\left(-\mathbf{p}^2/2Tm\right)$$

is the Maxwell momentum distribution of a particle with mass m , and $\Delta(\rho)$ is a normalized probability distribution like a"smoothed delta-function". We then want to reveal how probability distribution of BP's position $\boldsymbol{R}$ evolves after start from $\Delta(\boldsymbol{R} - \boldsymbol{R}_0)l$.

III. COLLISIONAL REPRESENTATION

If our fluid is a sufficiently dilute gas, or the Boltzmann-Grad gas, then inter-particle interactions can be described in terms of well separated collisions. Since any "collision" is a finite duration process, while the distribution functions (DF) F_n describe instant states of the system, we should reformulate DFs and equations (1) in terms of collision processes.

In principle, this is very simple task. First of all, let us consider the $(n+1)$-particle Poisson bracket, $[H_n, F_n]$, describing separate evolution of a group of n fluid atoms plus BP, and divide it into two parts, one of which describes drift of the center of mass of the group while another relative displacement of particles inside the group:

$$[H_n, F_n] \,=\, -\boldsymbol{V}_n \cdot \frac{\partial F_n}{\partial \boldsymbol{Z}_n} - \frac{\partial F_n}{\partial \Theta_n} \qquad (3)$$

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We introduced the center of mass positions and velocities,

$$\mathbf{Z}_n = \frac{M\mathbf{R}+m\sum_{j=1}^{n}\mathbf{r}_j}{M+nm}\ , \quad \mathbf{V}_n = \frac{\mathbf{P}+\sum_{j=1}^{n}\mathbf{p}_j}{M+nm}\ ,$$

and (for $n>0$) the inner time of the relative motion, Θ_n. For example, at $h=1$,

$$-\frac{\partial F_1}{\partial \Theta_1} \ = \ -\boldsymbol{u}_1\cdot\frac{\partial F_1}{\partial \rho_1} + \Phi_b'(\rho_1)\cdot\left[\frac{\partial F_1}{\partial \mathbf{p}_1}-\frac{\partial F_1}{\partial \mathbf{P}}\right]$$

with $\rho_1=\boldsymbol{r}_1-\boldsymbol{R}$ and $\boldsymbol{u}_1=\boldsymbol{v}_1-\boldsymbol{V}$.

Second, let a given relative disposition of the particles can be qualified as a section of collision process (pair collision at $n=1$ or sequence of n connected pair collisions). Then it is reasonable to treat corresponding DF F_n as a measure of mean (ensemble average) density of such processes, and consider it as a function of $t,\mathbf{Z}_n,\mathbf{V}_n,\Theta_n$, n relative incoming (in-state) velocities (e.g. $\boldsymbol{u}_j=\boldsymbol{v}_j-\boldsymbol{V}$) and $3n-1$ input geometric parameters of the process.

Third, however, such the treatment can not be literal: if $F_n(t,\Theta_n,...)$ at time moment t represents "density of collisions" at this time, then its value at $t+\Delta t$ is not $F_n(t+\Delta t,\Theta_n,...)$ but $F_n(t+\Delta t,\Theta_n+\Delta t,...)$, since the same collision is represented by different Θ_n values at different times.

This statement means that if DF F_n really describe collisions as the whole processes then each of Eqs.1 for them (at $n>0$ must divide into two equations:

$$\frac{\partial F_n}{\partial t} = -\boldsymbol{V}_n\cdot\frac{\partial F_n}{\partial \boldsymbol{Z}_n} + \nu\frac{\partial}{\partial \mathbf{P}}\int_{n+1}\Phi_b'(\mathbf{R}-\mathbf{r}_{n+1})\,F_{n+1} + \\ +\nu\sum_{j=1}^{n}\frac{\partial}{\partial \mathbf{p}_j}\int_{n+1}\Phi_a'(\mathbf{r}_j-\mathbf{r}_{n+1})\,F_{n+1}\ , \qquad (4)$$

$$\frac{\partial F_n}{\partial \Theta_n} \ = \ 0\ , \qquad (5)$$

so that Eq.5 must be satisfied "inside collisions" (i.e. space-time regions assigned, in relative coordinates, to a collision process) while Eq.8 "out of collisions". It is natural: since relative movement of colliding particles is included, along with their interaction, into collisions, it is excluded from description of collision events as the wholes (for details and more explanations, see [1–3, 7]).

Fourth, the Eqs.5 are the tool for transforming the interaction integrals in Eq.8 into usual Boltzmannian "collision integrals":

$$\frac{\partial F_n}{\partial t} \ = \ -\boldsymbol{V}_n\cdot\frac{\partial F_n}{\partial \boldsymbol{Z}} + \nu\,\widehat{S}^{\,b}_{n+1}\,F^{in}_{n+1} + \\ +\nu\sum_{j=1}^{n}\widehat{S}^{\,a}_{j\,n+1}F^{in}_{n+1}\ , \qquad (6)$$

where $\widehat{S}^{\,a}_{j\,k}$ and $\widehat{S}^{\,b}_{k}$ are the Boltzmann collision operators acting on j-th and k-th atoms' velocities and on BP's and k-th atom velocities, respectively, and DFs F^{in}_{n+1} describe such $(n+1)$-particle configurations when the "outer" $(n+1)$-th particle is just on the border of the collision.

Such the border configurations and corresponding DFs need in special consideration [1–3]. If the most (infinite) part of the gas stay in thermodynamic equilibrium during all (finite-time) evolution of initial (finite-range) disturbance of the equilibrium, then naturally

$$F^{in}_{n+1} \ = \ G_m(\boldsymbol{p}_{n+1})\int F_{n+1}\,d\boldsymbol{p}_{n+1}\ , \qquad (7)$$

and Eqs.6 transform into

$$\frac{\partial F_n}{\partial t} \ = \ -\boldsymbol{V}_n\cdot\frac{\partial F_n}{\partial \boldsymbol{Z}} + \nu\widehat{\Lambda}^b\int F_{n+1}\,d\boldsymbol{p}_{n+1} + \\ +\nu\sum_{j=1}^{n}\widehat{\Lambda}^a_j\int F_{n+1}\boldsymbol{p}_{n+1} \qquad (8)$$

with $\widehat{\Lambda}^{a,b}_j$ being the Boltzmann-Lorentz operators. The latter are defined by

$$\widehat{S}^{\,a}_{j\,n+1}\left[F(...\boldsymbol{p}_j...)\,G_m(\boldsymbol{p}_{n+1})\right] \ = \ \widehat{\Lambda}^a_j\,F(...\boldsymbol{p}_j...)$$
$$\widehat{S}^{\,b}_{n+1}\left[F(...\boldsymbol{P}...)\,G_m(\boldsymbol{p}_{n+1})\right] \ = \ \widehat{\Lambda}^b\,F(...\boldsymbol{P}...)$$

Relations (7) and hence Eqs.8 do express the "molecular chaos", but with those principal difference from the Boltzmann's one that here it concerns velocities of colliding particles only. What is for coordinates of the particles, they possess mutual statistical correlations, as far strong as strong is non-uniformity of the coordinates probability distributions (more comments see [1, 2, 10]).

Of course, the transition from Eqs.1 to Eqs.8 should be accompanied by corresponding transition from initial conditions (2) to their collisional representation:

$$F_n(t=0,\boldsymbol{Z},\boldsymbol{P},\boldsymbol{p}^{(n)}) \ = \\ = \int_{\Omega^h}\int\ \delta\left(\boldsymbol{Z}-\frac{M\boldsymbol{R}+m\sum_{j=1}^{n}\boldsymbol{r}_j}{M+nm}\right)\times \\ \times\,F_n(t=0,\boldsymbol{R},\boldsymbol{r}^{(n)},\boldsymbol{P},\boldsymbol{p}^{(n)})\,d\boldsymbol{R}\prod_{j=1}^{n}\frac{d\boldsymbol{r}_j}{\Omega} \ = \\ = \ \left(1+\frac{nm}{M}\right)\int_{\Omega^n}\Delta\left(\boldsymbol{Z}-\frac{m}{M}\sum_{j=1}^{n}\rho_j-\boldsymbol{R}_0\right)\times \\ \times\prod_{j=1}^{n}\frac{d\rho_j}{\Omega}\prod_{j=1}^{n}G_m(\boldsymbol{p}_j)\ ,$$

where $\rho_j=\boldsymbol{r}_j-\boldsymbol{Z}$ and Ω is a "collision volume", i.e. volume of a region assigned (in each of the spaces $\rho_j=\boldsymbol{r}_j-\boldsymbol{Z}$) per one collision. Thus under the Boltzmann-Grad limit, when a width of the distribution $\Delta(\rho)$ is krpt constant in units of λ we can write, obviously,

$$F_n(t=0,\boldsymbol{Z},\boldsymbol{P},\boldsymbol{p}^{(n)}) \ = \\ = \ \left(1+\frac{nm}{M}\right)\Delta(\boldsymbol{Z}-\boldsymbol{R}_0)\prod_{j=1}^{n}G_m(\boldsymbol{p}_j) \qquad (9)$$

This is generalization of initial conditions derived in [3], directly from the Gibbs canonical ensemble, for the case when BP is merely one of gas atoms.

Notice also that under the Boltzmann-Grad limit all the variety of the center of mass coordinates $\boldsymbol{Z}_n$ can be replaced by single common variable $\boldsymbol{Z}$.

IV. DIFFUSIVE EVOLUTION AND MORE SIMPLIFICATION OF EQUATIONS

The Eqs.8 still seem very complicated. Therefore we would like to further coarsen and simplify them being eventually interested in the distributions in configurational spaces,

$$W_n(t,\boldsymbol{Z}) \,=\, \int ... \int F_n \, d\boldsymbol{p}_1 ... d\boldsymbol{p}_n \, d\boldsymbol{P}$$

Since, according to Eqs.8,

$$\frac{\partial W_n}{\partial t} \,=\, -\frac{\partial \boldsymbol{Q}_n}{\partial \boldsymbol{Z}} \;\;, \tag{10}$$

where $\boldsymbol{Q}_n$ are corresponding probability flows,

$$\boldsymbol{Q}_n(t,\boldsymbol{Z}) \,=\, \int ... \int \boldsymbol{V}_n \, F_n \, d\boldsymbol{p}_1 ... d\boldsymbol{p}_n \, d\boldsymbol{P} \;\;,$$

we have to consider also at least evolution equation for these flows,

$$\frac{\partial \boldsymbol{Q}_n}{\partial t} \,=\, -\frac{\partial}{\partial \boldsymbol{Z}} \int ... \int \mathbf{V}_n \, \mathbf{V}_n \, F_n \; d\mathbf{p}_1 ... d\mathbf{p}_n \, d\mathbf{P} + \tag{11}$$

$$+ \int ... \int \mathbf{V}_n \left[\widehat{\Lambda}^b + \sum_{j=1}^{n} \widehat{\Lambda}_j^a \right] \, F_{n+1} \; d\mathbf{p}_1 ... d\mathbf{p}_{n+1} \, d\mathbf{P}$$

In order to express right-hand sides here via $\boldsymbol{Q}$'s and W_n's only and thus close the equations, we need in two assumptions. The first is that the conditional velocity distributions, F_n/W_n, duffer from the equilibrium ones only by non-zero ($\boldsymbol{Z}$-dependent) mean drift velocities, $\overline{\boldsymbol{V}}_n = \boldsymbol{Q}_n/W_n$],l which is common for all the velocities ($\boldsymbol{V}$ and $\boldsymbol{v}_j$) under consideration. This hypothesis, in turn, can be correct only under the second assumption, namely, that all the velocities possess equal relaxation rates. Formally, the equality

$$\boldsymbol{V}_n \left[\widehat{\Lambda}^b + \sum_{j=1}^{n} \widehat{\Lambda}_j^a \right] \,=\, -\,\gamma \, \boldsymbol{V}_n$$

approximately takes place, that is $\boldsymbol{P} = M\boldsymbol{V}$ and $\boldsymbol{p}_j = m\boldsymbol{v}_j$ are left eigenfunctions of operators $\widehat{\Lambda}^b$ and $\widehat{\Lambda}_j^a$, respectively, corresponding to the same eigenvalue $-\gamma$. Then, taking into account also the initial conditions (9), we can expect that

$$\int ... \int (\mathbf{V}_n)_i \, (\mathbf{V}_n)_j \; F_n \; d\mathbf{p}_1 ... d\mathbf{p}_n \, d\mathbf{P} \;\approx\; \frac{T\,\delta_{ij}}{M+nm} \, W_n \;\;,$$

as in equilibrium. Consequently Eqs.11 reduce to

$$\frac{\partial \boldsymbol{Q}_n}{\partial t} \,=\, -\frac{T}{M+nm} \, \frac{\partial W_n}{\partial \boldsymbol{Z}} - \gamma \, \boldsymbol{Q}_{n+1} \tag{12}$$

and close Eqs.10.

Of course, on one hand, the second of our assumptions looks rather unnatural, since in reality operators $\widehat{\Lambda}^b$ and $\widehat{\Lambda}_j^a$, may have very different eigenvalues. But, on the other hand, the corresponding approximation still allows to consider the case of different masses of BP and atoms, $M \neq m$l and thus obtain a generalization of results of [3].

Clearly, our approximation reflects the fact that the system "gas + BP" is non-equilibrium in statistical (or informational) sense only but not in literally thermodynamic sense, and therefore its evolution is sooner "diffusive" than "hydrodynamical". Nevertheless, if velocities of BP and atoms relax (and fluctuate) with different rates then their conditional distribution inside the collisional clusters can be significantly non-equilibrium (non-Gaussian), and we need in a more complicated approximation.

For the present let us confine ourselves by the Eqs,10 and 12. Initial conditions to them, as follow from (9), are

$$W_n(t=0,\boldsymbol{Z}) \,=\, \left(1+\frac{nm}{M}\right) \, \Delta(\boldsymbol{Z}-\boldsymbol{R}_0) \;\;, \tag{13}$$

$$\boldsymbol{Q}_n(t=0,\boldsymbol{Z}) \,=\, 0 \;\;,$$

where now, of course, we can merely $\delta(\boldsymbol{Z})$ in place of $\Delta(\boldsymbol{Z}-\boldsymbol{R}_0)$.

V. ANALYSIS OF SHORTENED EQUATIONS

As usually, let us make the Laplace and Fourier transforms, writing

$$F(p,\boldsymbol{k}) \,=\, \int_0^\infty dt \; e^{-p\,t} \int d\boldsymbol{Z} \; e^{i\boldsymbol{k}\cdot\boldsymbol{Z}} \, F(t,\boldsymbol{Z}) \;\;,$$

and introduce designations

$$V_0 = \sqrt{\frac{T}{M}} \;,\;\; v_0 = \sqrt{\frac{T}{m}} \;,\;\; D_b = \frac{V_0^2}{\gamma} \;,\;\; D_a = \frac{v_0^2}{\gamma} \;,$$

$$\alpha = \frac{m}{M} \;,\;\; X = \frac{V_0^2\,\boldsymbol{k}^2}{p^2} \;\;\;,$$

Then Eqs.10 and 12 together with Eq.13 yield

$$W_n(p,\boldsymbol{k}) = \frac{1+\alpha n}{p} \,+\, \frac{i\boldsymbol{k}}{p} \cdot \boldsymbol{Q}_n(p,\boldsymbol{k}) \;\;, \tag{14}$$

$$\left\{ 1 + \frac{X}{1+\alpha n} \right\} \boldsymbol{Q}_n(p,\boldsymbol{k}) = \frac{i\boldsymbol{k}\,V_0^2}{p^2} - \frac{\gamma}{p} \, \boldsymbol{Q}_{n+1}(p,\boldsymbol{k}) \tag{15}$$

According to characteristic structure of the chain of equations (15), its solution can be written as sum of infinite

iteration series. This yields

$$\boldsymbol{Q}_n = -\frac{i\boldsymbol{k}\,V_0^2}{p\gamma}\sum_{s=n}^{\infty}\prod_{r=n}^{s}\left(-\frac{\gamma}{p}\cdot\frac{1+\alpha r}{X+1+\alpha r}\right)\ ,$$

$$W_n = \frac{1+\alpha n}{p} + \frac{X}{\gamma}\sum_{s=n}^{\infty}\prod_{r=n}^{s}\left(-\frac{\gamma}{p}\cdot\frac{1+\alpha r}{X+1+\alpha r}\right) \qquad (16)$$

This is generalization of of the series from [3].

Next, let us introduce quantities

$$a = \frac{1}{\alpha} + n\ ,\quad ,\quad c = \frac{X}{\alpha} + \frac{1}{\alpha} + n = \frac{v_0^2\boldsymbol{k}^2}{p^2} + \frac{1}{\alpha} + n\ ,$$

and rewrite expression (16) as follows,

$$W_n = \frac{1+\alpha n}{p} + \frac{X}{\gamma}\sum_{s=1}^{\infty}\left(-\frac{\gamma}{p}\right)^s\frac{\Gamma(a+s)}{\Gamma(a)\,(s-1)!}\,B(c,n) =$$

$$= \frac{1+\alpha n}{p} + \frac{X}{\gamma}\sum_{s=1}^{\infty}\frac{(-\gamma/p)^s}{\Gamma(a)\,(s-1)!}\int_0^{\infty}x^{a+s-1}\,e^{-x}\,dx\ \times$$

$$\times\int_0^1 t^{n-1}\,(1-t)^{c-1}\,dt\ =$$

$$= \frac{1+\alpha n}{p}\left[1 - \frac{X}{\alpha}\int_0^1\frac{(1-t)^{c-1}}{(1+\gamma t/p)^{a+1}}\,dt\right]$$

Hence,

$$\frac{pW_n}{1+\alpha n} = 1 - \frac{X}{\alpha}\int_0^1\frac{(1-t)^{\frac{X}{\alpha}+\frac{1}{\alpha}+n-1}}{(1+\gamma t/p)^{\frac{1}{\alpha}+n+1}}\,dt \qquad (17)$$

which is direct generalization of formula (27) from [3].

VI. LARGE-SCALE ASYMPTOTIC

As we already know [1–3], most important statistical characteristics of the BP's random walk what distinguish it from the usual Ornstein-Uhlenbeck process or similar random processes) are its fourth-order path statistical moment or cumulant and long-range asymptotic of the path distribution. The latter is defined by

$$\overline{W}_n(p,\boldsymbol{k}) = \lim_{\xi\to 0}\,\xi^2\,W_n(\xi^2 p\,,\,\xi\,\boldsymbol{k})\ ,$$

$$\overline{\boldsymbol{Q}}_n(p,\boldsymbol{k}) = \lim_{\xi\to 0}\,\xi\,\boldsymbol{Q}_n(\xi^2 p\,,\,\xi\,\boldsymbol{k})$$

(for details see [3]). We just foreknow that our random walk behaves similar;y to diffusion processes (like the Wiener process) but with randomly varying diffusivity in place of a constant one. Taking into account results of [3], it is reasonable to interpret the asymptotic in terms of slow (scaleless) diffusivity fluctuations. Correspondingly, let us write

$$\overline{W}_n = (1+\alpha n)\int_0^{\infty}\frac{\overline{U}_n(D)\,dD}{p + D\boldsymbol{k}^2}\ , \qquad (18)$$

where $\overline{U}_n(D)$ is effective normalized probability distribution of diffusivity (at $n=0$ it represents BP's diffusivity while at $n>0$ characterizes spreading of densities of two- and multi-particle collisional events).

In the mentioned limit the expression (17) turns to

$$\frac{\overline{W}_n}{1+\alpha n} = \left[\frac{1}{\alpha}+n+1\right]\frac{1}{p}\int_0^{\infty}\frac{\exp\left(-\frac{pX}{\gamma\alpha}\,y\right)}{(1+y)^{\frac{1}{\alpha}+n+2}}\,dy$$

or equivalently

$$\frac{\overline{W}_n}{1+\alpha n} = \left[\frac{1}{\alpha}+n+1\right]\int_0^{\infty}\frac{\exp\left(-D_a\boldsymbol{k}^2\tau\right)d\tau}{(1+p\tau)^{1/\alpha+n+2}} \qquad (19)$$

Combining it with identity

$$1/(1+y)^{b+1} = \int_0^{\infty}x^b\,e^{-(1+y)x}\,dx/\Gamma(b+1)\ ,$$

with $b = 1/\alpha + n + 1$, it is easy to obtain

$$\frac{\overline{W}_n}{1+\alpha n} = \frac{1}{\Gamma(b)}\int_0^{\infty}\frac{x^b\exp(-x)\,dx}{px + D_a\boldsymbol{k}^2}$$

Comparison of this formula and (18) yields

$$\overline{U}_n(D) = \frac{1}{\Gamma(b)\,D}\left(\frac{D_a}{D}\right)^b\exp\left(-\frac{D_a}{D}\right) \qquad (20)$$

with $b = 1/\alpha + n + 1 = \frac{M}{m} + n + 1$.

Hence, the effective long-range diffusivities are random quantities with very bad statistics. In particular, its their most probable (m.p.) and mean values essentially differ one from another:

$$(\,\mathtt{m.\,p.}\ D\,)_n = \frac{D_a}{2 + M/m + n}\ ,\quad \langle D\rangle_n = \frac{D_a}{M/m+n}$$

Notice that $\langle D\rangle_n = D_b$.

Making in (18) the inverse Laplace and Fourier transforms and substituting (20), in the space-time representation we have

$$\overline{W}_n(t,\boldsymbol{R}) \equiv \lim_{s\to\infty}\,s^d\,W_n(s^2t, s\boldsymbol{R}) = \qquad (21)$$

$$= \int_0^{\infty}(4\pi Dt)^{-d/2}\exp\left(-\frac{\boldsymbol{R}^2}{4Dt}\right)\overline{U}_n(D)\,dD\ =$$

$$= \frac{\Gamma(b+d/2)}{(4\pi D_a t)^{d/2}\ \Gamma(b)\ (1+\boldsymbol{R}^2/4D_a t)^{\,b+d/2}}\ ,$$

where $b = 1/\alpha + 1 + n = M/m + 1 + n$, $\boldsymbol{R}\equiv\boldsymbol{Z}$, and d is the space dimension ($d=3$).

VII. STATISTICAL MOMENTS AND 1/F NOISE

Expansion of the $W_n(p,\boldsymbol{k})$ into series over $\boldsymbol{k}^2$ gives Laplace transforms of equilibrium statistical moments of the distributions $W_n(t,\boldsymbol{R})$:

$$\frac{W_n(p,k)}{1+\alpha n} = \frac{1}{p} + \sum_{s=1}^{\infty}\frac{(-k^2)^s}{(2s)!}\int_0^{\infty}e^{-p\,t}\,\langle R^{2s}(t)\rangle_n\,dt \qquad (22)$$

Here and be;ow $R(t)$ means projection of vector $\boldsymbol{R}(t)$ onto arbitrary fixwd axis and

$$\langle R^{2s}(t)\rangle_n = \int R^{2s}\, W_n(t,\boldsymbol{R})\, d\boldsymbol{R}$$

Direct comparison of (22) with (17) shows that

$$\int_0^\infty e^{-p\,t}\,\langle R^{2s}(t)\rangle_n\, dt \;=\; \frac{(2s)!}{(s-1)!}\cdot\frac{1}{p}\left(\frac{v_0^2}{p^2}\right)^s \times \qquad (23)$$
$$\times\int_0^1 \frac{(1-x)^{1/\alpha+n-1}}{(1+\gamma x/p\,)^{1/\alpha+n+1}}\left[\ln\frac{1}{1-x}\right]^{s-1} dx$$

Considering the long-time asymptotic of these expressions, i.e. the limit $p/\gamma\to 0$, we have, firstly,

$$\int_0^\infty e^{-p\,t}\,\langle R^2(t)\rangle_n\, dt \to \frac{2V_0^2}{(1+\alpha n)p^2\gamma} = \frac{2D_b}{(1+\alpha n)p^2} \quad (24)$$

which corresponds to the usual diffusion-law asymptotic $\langle R^2(t)\rangle_n \to 2D_b t/(1+\alpha n)$ at $\gamma t\to\infty$.

Secondly, an asymptotic behavior of the fourth-order moment crucially depends on sign of $M/m+n-1$. Namely, if this quantity <1, that is $n=0$ and $M/m<1$, then

$$\int_0^\infty e^{-p\,t}\,\langle R^4(t)\rangle_0\, dt \to \frac{24D_b^2}{p^3}\left[\frac{\gamma}{p}\right]^{1-M/m} C\left(\frac{M}{m}\right)\,, \quad (25)$$

$$C(z)\;\equiv\; z^2\int_0^1 \frac{(1-x)^{z-1}}{x^{\,z+1}}\,\ln\frac{1}{1-x}\;dx \;=\frac{\pi z}{\sin\pi z} \qquad (26)$$

At $n=0$ and $M/m=1$, we come to result of [3],

$$\int_0^\infty e^{-p\,t}\,\langle R^4(t)\rangle_0\, dt \to \frac{24D_b^2}{p^3}\ln\frac{\gamma}{p} \qquad (27)$$

And at $M/m>1$ under $n=0$ we find

$$\int_0^\infty e^{-p\,t}\,\langle R^4(t)\rangle_0\, dt \to \frac{24D_b^2}{p^3}\cdot\frac{M}{M-m} \qquad (28)$$

These three asymptotics should be compared with $24D_b^2/p^3$ which is asymptotic of $\langle R^4(t)\rangle_0$ for the ideal Gaussian random walk.

What is for the higher-order moments at $n=0$ and any moments at $n>0$, they are presented by table

$$\int_0^\infty e^{-p\,t}\,\langle R^{2s}(t)\rangle_n\, dt \to \frac{(2s)!}{(s-1)!}\cdot\frac{1}{p}\left(\frac{v_0^2}{p^2}\right)^s \times \quad (29)$$
$$\times\left[\frac{p}{\gamma}\right]^{b+1}\int_0^1\frac{(1-x)^{b-1}}{x^{\,b+1}}\left[\ln\frac{1}{1-x}\right]^{s-1}dx \quad \texttt{if}\;\; s>b+1$$
$$\times\quad\left(\frac{p}{\gamma}\right)^s\ln\frac{\gamma}{p} \qquad\qquad\qquad \texttt{if}\;\; s=b+1$$
$$\times\qquad\left(\frac{p}{\gamma}\right)^s\frac{\Gamma(s)\Gamma(b+1-s)}{\Gamma(b+1)} \qquad \texttt{if}\;\; s<b+1$$

with $b=1/\alpha+n$. The first row here shows that high enough moments are determined by not only the characteristic diffusion lengths $\sqrt{2D_b t}$ and $\sqrt{2D_a t}$ but also by free-flight lengths $V_0 t$ and v_0.

In the time domain, the asympt0tic behavior of fourth0order cumulamt of BP's path what corresponds to (25)-(28) is

$$\langle R^4(t)\rangle_0 - 3\langle R^2(t)\rangle_0^2 \to \qquad (30)$$
$$\to\; 3\,(2D_b^2t)^2\,(\gamma t)^{1-M/m}\,\frac{2C(M/m)}{\Gamma(4-M/m)} \quad \texttt{if}\;\; \frac{M}{m}<1$$
$$\to\; 3\,(2D_b^2t)^2\,\ln(\gamma t) \quad \texttt{if}\;\; \frac{M}{m}=1$$
$$\to\; 3\,(2D_b^2t)^2\,\frac{m}{M-m} \quad \texttt{if}\;\; \frac{M}{m}>1$$

Interpreting these asymptotics as manifestation of low-frequency fluctuations of BP's diffusivity, we see that in any case (i.e. at any mass ratio M/m) that are non-ergodic fluctuations represented by formally non-stationary random processes, in the sense explained in [1]. Corresponding effective spectral densities of the diffusivity fluctuations at frequencies $\ll\gamma$ are

$$S_D(\omega)\to\;\frac{2\pi D_b^2}{\omega}\left[\frac{\gamma}{\omega}\right]^{1-\frac{M}{m}}\times \qquad (31)$$
$$\times\,\frac{M/m}{(3-\frac{M}{m})(2-\frac{M}{m})\cos\left[\frac{\pi}{2}\left(1-\frac{M}{m}\right)\right]} \quad \texttt{if}\;\; \frac{M}{m}<1$$
$$S_D(\omega)\to\;\frac{\pi D_b^2}{\omega} \quad \texttt{if}\;\; \frac{M}{m}=1$$
$$S_D(\omega)\to\;2\pi D_b^2\,\delta(\omega)\,\frac{m}{M-m} \quad \texttt{if}\;\; \frac{M}{m}>1$$

The latter expression means "static" fluctuations instead of a random process. pe, this is consequence of approximate character of our consideration, while the exact one would change the factor $\delta(\omega)$ to something like $\omega^{-1}\ln^\beta(\gamma/\omega)$.

At last, consider asymptotic of sufficiently high-order moments. Namely, at $s>b=1/\alpha+n+1=M/m+n+1$ from (23) we have

$$\int_0^\infty e^{-p\,t}\,\langle R^{2s}(t)\rangle_n\, dt \;\to\; \frac{(2s)!}{(s-1)!}\cdot\frac{1}{p}\left(\frac{D_a}{p}\right)^b\left(\frac{v_0^2}{p^2}\right)^{s-b}\times$$
$$\times\int_0^1\frac{(1-x)^{b-2}}{x^b}\left[\ln\frac{1}{1-x}\right]^{s-1}dx$$

and correspondingly

$$\langle R^{2s}(t)\rangle_n \;\to\; (D_a t)^b\,(v_0^2t^2)^{s-b}\;\times \qquad (32)$$
$$\times\,\frac{(2s)!}{(s-1)!\,\Gamma(2s-b)}\int_0^1\frac{(1-x)^{b-2}}{x^b}\left[\ln\frac{1}{1-x}\right]^{s-1}dx$$

The coefficient here can be estimated as

$$\frac{\langle R^{2s}(t)\rangle_n}{(D_a t)^b\,(v_0^2t^2)^{s-b}} \;< \qquad (33)$$
$$<\;\frac{(2s)!}{(s-1)!\,\Gamma(2s-b)}\int_0^\infty y^{s-b-1}\,(1+y)^b\,e^{-(b-1)y}\,dy$$

Hence, for fixed $b = M/m + n + 1$ and large enough t we can write

$$\lim_{s\to\infty} \langle R^{2s}(t)\rangle_n^{1/s} \lesssim \frac{v_0^2 t^2}{M/m+n}$$

This means that the distributions $W_n(tl\boldsymbol{R})$ are sharply cut off at characteristic ballistic-flight lengths $|\boldsymbol{R}| \sim t\sqrt{T/(M+nm)}$. In particular, the BP's path distribution $W_0(tl\boldsymbol{R})$ is cut off at $|\boldsymbol{R}| \sim V_0 t$.

VIII. VIRIAL RELATIONS

In conclusion let us concentrate on W_n's dependence on the gas density ν. Obviously, it is the same as dependence on γ, since $\gamma \propto \nu$ is the only ν-dependent parameter of our model, and therefore $\gamma\partial/\partial\gamma = \nu\partial/\partial\nu$.

From Eq.17 it follows that

$$\frac{W_{n+1}}{1+\alpha(n+1)} = \left[1 + \frac{1+p/\gamma}{1/\alpha+n+1}\,\nu\frac{\partial}{\partial\nu}\right]\frac{W_n}{1+\alpha n} \quad (34)$$

In the long-range limit it turns into

$$\frac{\overline{W}_{n+1}}{1+\alpha(n+1)} = \left[1 + \frac{1}{1/\alpha+n+1}\,\nu\frac{\partial}{\partial\nu}\right]\frac{\overline{W}_n}{1+\alpha n} \quad (35)$$

At that, in application to (20), we cam make change $\nu\partial/\partial\nu = -D_b\partial/\partial D_b - D_a\partial/\partial D_a$.

In essence, formulas (34)-(35) represent straight analogy of the "virial relations" investigated in [4–8] on rigorous and most general level. Special treatment of relations like (35) will be done elsewhere.

IX. RESUME

In this paper, following [1] and [3], we continued approximate analysis of general equations of the collisional approximation to kinetics of spatially non-uniform gas [1] (see also Sec.III above and [2], [3] and [9]). We extended method of [3] ("'diffusive approximation") to the case when the test "Brownian" particle (BP) has a mass different from mass of the gas atoms, although posse the same friction, or momentum relaxation rate, as the atoms. By the example of this specific but interesting situation we demonstrated that both the spectrum of low-frequency 1/f-type fluctuations in BP's diffusivity and effective (time-smoothed) probability distribution of the diffusivity essentially depend on the mass ratio of BP and atoms. This means that probability distribution of BP's path depends on this ratio, at that always possessing essentially non-Gaussian diffusive long-range asymptotic.

In the case we considered under the approximation we used the diffusivity 1/f-type, or "flicker", noise has the exponent equal to or greater than unit. It remains unclear whether molecular random walk in a gas (or in a liquid) can have exponents less than unit or at least "a little less" as in the phenomenological theory suggested in [12, 13] for charge transport (see also [2]). To answer this question and consider more general situations (first of all the case of different relaxation rates) we should leave the just exploited approximation (since it presumes presence of quasi-equilibrium inside the "collisional clusters) and start again from the equations (8) [1] or even from formally exact equations of molecular Brownian motion (see Sec.II and [4, 5]).

[1] Yu. E. Kuzovlev, "Bogolyubov-Born-Green-Kirkwood-Yvon equations, self-diffusion and 1/f-noise in a slightly nonideal gas", Sov.Phys.-JETP, **67** (12), 2469 (1988) [in Russian: Zh.Eksp.Teor.Fiz., **94**, No.12, 140 (1988)]. The author's translation of this work is placed to arXiv: 0907.3475 .

[2] Yu. E. Kuzovlev, arXiv: cond-mat/9903350.

[3] Yu. E. Kuzovlev, arXiv: cond-mat/0609515 .

[4] Yu. E. Kuzovlev, "Molecular random walk and a symmetry group of the Bogoliubov equation" Theoretical and Mathematical Physics **160** (3) 1300-1314 (Sep. 2009) {DOI:10.1007/s11232-009-0117-0}.

[5] Yu. E. Kuzovlev, arXiv : 0810.5383 , 0908.0274 .

[6] Yu. E. Kuzovlev, arXiv: 0705.4580, 0710.3831, 0803.0301 .

[7] Yu. E. Kuzovlev, arXiv: 0802.0288 .

[8] Yu. E. Kuzovlev, arXiv: 1001.1558 .

[9] Yu. E. Kuzovlev, arXiv: 1006.1505 .

[10] Yu. E. Kuzovlev, arXiv: 0612325 .

[11] N. N. Bogolyubov. Problems of dynamical theory in statistical physics. North-Holland, 1962.

[12] Yu. E. Kuzovlev and G. N. Bochkov, "Radiophysics and Quantum Electronics", No.3 (1983) [in Russian: Izv. VUZov.-Radiofizika, **26**, 310 (1983)]; *ibid.*, No.9 (1984) [in Russian: *ibid.*, **27**, 1151 (1984)].

[13] G. N. Bochkov and Yu. E. Kuzovlev, "New in 1/f-noise studies", Sov.Phys.-Usp., **26**, 829 (1983) [in Russian: UFN, **141**, 151 (1983)].